Stability Studies of Biodiesel

E. Natarajan

Mechanical Engg. Department, Anna University, Chennai, India

enatarajan123@gmail.com

***Abstract*- Oxidation stability of biodiesel is an important issue because fatty acid derivatives are more sensitive to oxidative degradation than mineral fuel. The vegetable oil, fats and their biodiesel suffer with the drawback of deterioration of its quality during long term storage unlike petroleum diesel due to large number of environmental and other factors making the fuel stability and quality questionable. There are various types of stabilities like oxidation, storage and thermal, playing key roles in making the fuel unstable. The present paper is an attempt to review the work done so far on the oxidation and thermal stability of biodiesel under different conditions. The effect of antioxidants on the stability parameters has also been reviewed in the present paper.**

Keywords*- *Fatty Acid; Oxidation Stability; Thermal Stability

I. INTRODUCTION

Biodiesel is a mixture of fatty acid monoalkyl esters with relatively high concentrations of long-chain mono and polyunsaturated compounds to promote better cold flow properties [1, 2, 3]. Methyl esters from Sunflower oil (SME), for example, are typically composed of mainly C-16 and C-18, where 80–85 % (w/w) of the total mixture is unsaturated FAME [4]. The presence of such mono and polyunsaturated compounds make ME highly susceptible to oxidative degradation [5].

Transesterification reaction of oil or fats with short chain alcohol usually methanol and ethanol, leads to the production of mixture of corresponding mono-alkyl esters defined as biodiesel. Since the biodiesel has the fatty acids compositions similar to the parent oils or fats with considerable amount of unsaturated fatty acids, its oxidative stability is affected, especially during its long-time period storage [6, 7]. Exposure to ultraviolet radiation (UV) irradiation, high temperature and presence of metal traces (contaminants) can reduce the overall stability of the biofuel, thereby, affecting its quality and hence marketability. The stability parameters of the biodiesel like kinematic viscosity, cetane number and acid value are affected during oxidative degradation [6, 8, 9].

Apart from a number of parameters affecting the stability of vegetable oils as well as biodiesel, the temperature has significant effect on oxidative degradation, perhaps, due to the enhancement in the rate of degradation thereby playing an important role in destabilizing the fuel quality which is the subject of the present paper. Thermal Stability involves the measurement of the tendency of a fuel to produce asphaltenes, when exposed to high temperature conditions. These asphaltenes are tar like resinous substances generated in the fuel and plug the fuel filters of the engines when used as fuel [10].

A. Mechanism of Oxidation Stability

Primary oxidation Peroxidation occurs by a set of reactions categorized as initiation, propagation, and termination [12] as in Fig. 1, which shows that first set involves the removal of hydrogen from a carbon atom to produce a carbon free radical. If diatomic oxygen is present, the subsequent reaction to form a peroxy radical becomes extremely fast even not to allow significant alternatives for the carbon-based free radical. The peroxy free radical is not reactive compared to carbon free radical, but is sufficiently reactive to quickly abstract hydrogen from a carbon to form another carbon radical and a hydroperoxide (ROOH). The new carbon free radical can then react with diatomic oxygen to continue the propagation cycle. This chain reaction terminates when two free radicals react with each other to yield stable products.

Initiation: $RH + I \rightarrow R\cdot + IH$

Propagation: $R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

Termination: $R\cdot + R\cdot \rightarrow R\text{-}R$

$ROO\cdot + ROO\cdot \rightarrow$ Stable Products

Fig. 1 Primary oxidation reaction

B. Mechanism of Thermal Stability

At sufficiently high temperatures, the methylene-interrupted polyunsaturated olefin structure will begin to isomerize to more stable conjugated structure. Once this isomerization has begun, a conjugated diene group from one fatty acid chain can react with a single olefinic group from another fatty acid chain to form a cyclohexene ring [11, 12]. This reaction between a conjugated di-olefin and a mono-olefin group, called Diels Alder reaction and shown in Fig. 2 is known as Diels- Alder Reaction which becomes important at temperatures of 250°-300°C or more and the reaction products formed are called dimmers [13, 14, 15].

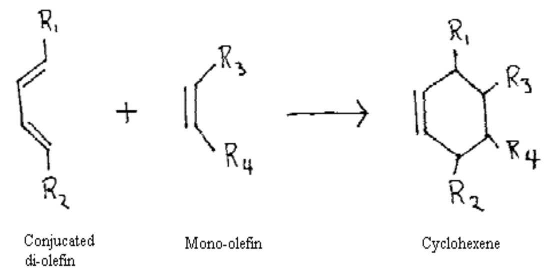

Fig. 2 Diels alder reaction

Thermal polymerization can also form trimers by the reaction of an isolated double bond in a dimer side chain with a conjugated diene from another fatty oil or ester molecule (a Diels Alder reaction) [15]. However, an earlier study provided the evidence supporting the non-Diels Alder coupling of two side chain olefin groups from a dimer and a fatty oil molecule [13]. Thermal polymerization is characterized by rapid reduction in total unsaturation as all the three olefin groups become one. When linseed oil was thermally polymerized at 300°C, initial polymerization resulted in dramatic reduction of total unsaturation as measured by IV. However, no increase in

molecular weight was observed. This was found to be due to an intra-molecular Diels Alder reaction between two fatty acid chains in the same triacylglyceride molecule. This may have ramifications for biodiesel made from used cooking oils that are subjected to temperatures in excess of 300°C when used in high pressure cookers. If such intramolecular dimers were to form during such thermal stressing, they would retain their linking when transesterified to methyl esters for use as biodiesel. The resulting species would be a di-ester with a molecular weight about twice that of a normal biodiesel ester molecule. If such biodiesels (i.e. yellow greases) were not distilled, these dimers would appear in the final fuel. No work has however been reported that indicates the presence of such dimers in used cooking oils and if so, their effect on fuel properties of the corresponding non-distilled biodiesel fuels. The potential existence of such dimeric species in non-distilled yellow grease biodiesel has not been addressed in the published literature pertaining to the U.S. biodiesel manufacturing/marketing industry [15].

The thermal polymerization may be of limited importance in biodiesel, which is heated repeatedly by the engine and recycled to the fuel tank before actual combustion. The thermal polymerization therefore does not impact the storage stability of biodiesel.

II. EFFECT OF HIGH TEMPERATURE ON BIODIESEL STABILITY

Vegetable oils consist of natural antioxidants that tend to increase the stability of fuel but as the vegetable oils are subjected to higher temperature conditions, the natural antioxidants present in the oil start deteriorating at a faster rate, thereby, decreasing its stability. As the biodiesel comes in contact with engine, it gets heated leading to the decrease in fuel stability.

Paolo et al. [16] evaluated the storage stability of biodiesel at different temperatures. Samples were kept at two different temperatures (20^0C and 40^0C) during experimentation and it was found that increase in PV was higher at lower temperature while using the same container.

Dunn [17] has evaluated the effect of oxidation under accelerated conditions on fuel properties of methyl soyate. SME samples were collected from four different fuel producers. Oxidation reactions were conducted in the laboratory under varying time and temperature conditions. In order to determine the effect of oxidative degradation on biodiesel fuel, the reaction conditions were designed to produce measurable changes in most fuel properties in a relatively short time. Samples were placed in a thrsee-necked round-bottomed flask and heated by a variac controlled mantle. Clean and dry air was bubbled slowly throughout the reaction using water-cooled condenser to minimize the evaporative losses. Air flow was manually regulated at a constant rate of 0.5 standard cm^3/min(SCCM) with stirring of the reaction mixture to minimize wall effects and to keep the mixture homogeneous throughout the duration of the reaction. The results indicated that with increase in reaction temperature, viscosity, acid value and peroxide value respectively increased significantly including specific gravity whereas, the cold flow properties were minimally affected for temperature up to 150^0C.

Xin et al. [18] studied the oxidation stability of biodiesel prepared from supercritical methanol method. The effect of temperature on the tocopherol content in biodiesel was studied by choosing rapeseed biodiesel as a representative biodiesel.

The biodiesel obtained through supercritical method will therefore have overall lower stability compared to biodiesel prepared using other methods of transesterification [16, 18, 19, 20].

Dunn [19] studied the effect of temperature on the oil stability index (hrs) of biodiesel and found that an increasing temperature accelerated the oxidation reaction causing a decrease of OSI.

Nzikou et al. [20] studied the thermal stability of vegetable oils during frying and found a decrease in Linoleic acid contents with increase in frying hours of oil.

Relationship between % linoleic acid with frying hrss for SO and MO frying temperature of 180^0C indicates that the linoleic content decreases with increase in frying hrss due to lipid oxidation [20].

A. Antioxidants

Oxidation cannot be entirely prevented but can be significantly slowed down by the use of antioxidants which are chemicals that inhibit the oxidation process. Two types of antioxidants are generally known: chain breakers and hydroperoxide decomposers [21]. Literature related to hydroperoxide decomposers is very scarce. The two most common types of chain breaking antioxidants are phenolic and amine-types. Almost all the work related to stability of fatty oil and ester applications is limited to the phenolic type of antioxidant. The mechanism of all chain breaking antioxidants is shown below in Fig. 3.

$$ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$$

$$A^{\cdot} \rightarrow \text{stable product}$$

Fig. 3 Mechanism of all chain breaking antioxidants

As can be seen, the antioxidant contains a highly labile hydrogen that is more easily abstracted by a peroxy radical than fatty oil or ester hydrogen. The resulting antioxidant free radical is either stable or further reacts to form a stable molecule which is further resistant to chain oxidation process. Thus the chain breaking antioxidants interrupt the oxidation chain reaction in order to enhance stability.

The effectiveness of antioxidant is generally measured by stressing a fatty oil or ester molecule both with and without the antioxidant.

B. Synthetic Antioxidants

These antioxidants are added in oils or biodiesel to increase its stability. Some of the most common synthetic antioxidants are given in Table 1.

TABLE I COMMONLY USED ANTIOXIDANTS

S. No.	Antioxidants	Abbraviations
1	Pyrogallol	PY
2	Gallic acid	GA
3	Propyl gallate	PG
4	Butylated hydroxyanisole	BHA
5	Butylated hydroxyanisole	BHT
6	tert-Butyl hydroquinone	TBHQ

Different synthetic antioxidants had different effects on the stability of biodiesel, depending on the feed stock without affecting the properties such as viscosity, cold filter plugging point (CFPP), density, carbon residue and sulfated ash except acid value that appears to be affected slightly by the addition of antioxidants [22,23].

Mittelbach et al. [22] has further studied the Influence of Antioxidants on the Oxidation Stability of Biodiesel and showed the influence of different synthetic and natural antioxidants on the oxidation stability using the specified test method. The induction periods of methyl esters from rapeseed oil, used frying oil and tallow were found to improve significantly with PY, PG, and TBHQ, whereas BHT was not very effective.

Schober et al. [23] has experimented the potential of 11 different synthetic phenolic antioxidants to improve the oxidation stability of biodiesel prepared from different feedstocks. Variation of antioxidant concentrations between 100 and 1000 mg/kg showed that the efficiency of the antioxidants varied depending on the different types of biodiesel.

Liang et al [24] reported the effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. Crude palm oil methyl ester containing not less than 600 ppm of vitamin E were found to exhibit oxidative stability of more than 6 h and thus, conform to the specification of the European standard for biodiesel (EN 14214). While distilled palm oil methyl ester need to be treated with antioxidants in order to meet the specification. Synthetic antioxidants, namely BHT and TBHQ are found to be more effective than natural antioxidant, a-T in terms of their performance to enhance the RIP of DPOME.

Sarin et al. [25] has investigated the effect of two phenolic antioxidants namely 2, 6-ditertiarybutyl hydroxytoluene (AO-1), bis-2, 6- ditertiarybutyl phenol derivative (AO-2), and aminic antioxidant octylated butylated diphenyl amine (AO-3) on the oxidation stability of Jatropha curcas biodiesel. It is found that minimum dosing of 200 ppm of AO-1 was needed to improve the IP of neat JBD from 3.95 h to above 6 h as required by EN-14112 specification for biodiesel oxidation stability.

Domingos et al. [26] has experimented the influence of BHA, BHT and TBHQ in the oxidation stability of soyabean oil ethyl esters (biodiesel) and reported that BHT displayed the greatest efficacy in concentrations ranging from 200 to 7000ppm. Sendzikiene et al. [27] studied the oxidation stability of biodiesel produced from fatty wastes and suggested that the optimal level of synthetic antioxidants such as BHA and BHA for stabilization of fatty acid methyl esters was determined to be 400 ppm.

III. CONCLUSION

The review of the work done so far has revealed that biodiesel is more prone to oxidation when exposed to higher temperature due to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insolubles, gum and sediment in the biodiesel, which may often be responsible for fuel filter plugging, injector fouling, deposits formation in engine combustion chamber and various components of the fuel system. Large numbers of studies were devoted to the oxidation and thermal stability of different oils using these methods. Much effort is required to be done in the field of biodiesel especially, increase in the thermal/ oxidation stability of biodiesel from non- edible oils. Also the effect of blending of biodiesel with diesel on oxidation and thermal stability needs to be checked.

REFERENCES

[1] Jain S, Sharma MP. Prospects of biodiesel from Jatropha in India: A review. Renew Sust Energ Rev 2010; 14(2): 763- 771.

[2] Jain S, M.P. Sharma, Evaluation of Engine Performance on Biodiesel from Waste Cooking Oil. Presentated at the 4th international conference on “Energy Informatics and Cybernetics (EIC-2008)” held at Orlando, Florida, USA between June 29- July 02, 2008.

[3] Sharma MP and Agarwal R, Non-edible Oils as Potential Resources of Biodiesel. In Proceedings of 23rd National Convention of Chemical Engineers on Recent Trends in Chemical Engineering held on Oct. 5-7, 2007 at Chemical Engineering Department, IIT Roorkee ; 2007: 202-211.

[4] Knothe G, Van Gerpen J, Krahl J, the biodiesel handbook, AOCS Press, champaign 2005; 12: 281.

[5] Gunstone, F.D., Non-food uses of vegetable oils and their fatty acids, Industrial uses of soy oil for tomorrow, special report 96, Iowa State University 1995; 17-31.

[6] Knothe G, Some aspects of biodiesel oxidative stability, Fuel Process Technol 2007; 88: 669-77.

[7] Barnwal BK, Sharma MP, Prospects of Biodiesel Production from Vegetables Oils in India. Renew Sust Energ Rev 2005; 9: 363–378.

[8] Dunn RO, oxidative stability of biodiesel by dynamic mode pressurized differential scanning calorimetry (P-DSC), Transactions of the American Society of Agricultural and Biological Engineers 2006; 49(5): 1633-1641.

[9] Pinto AC, Guarieiro LLN, Rezende MJC, Ribeiro NM, Torres EA, Lopes WA, Pereira PAD and de Andrade JB, Biodiesel: An overview, J Braz Chem Soc 2005; 16 (6B):1313-1330.

[10] Schober S and Mittelbach M. Influence of diesel particulate filter additives on biodiesel quality. Eur J Lipid Sci Tech 2005; 107 (4): 268–271.

[11] Joyner NT and McIntyre JE. The Oven Test as an Index of Keeping Quality. Oil Soap 1938; 15: 184-186.

[12] Formo MW, Jungermann E, Noris F and Sonntag NOV. Bailey’s Indust Oil Fat Products, John Wiley and Son 1979; 1(4): 698-711.

[13] Jain S, Sharma MP. Stability of biodiesel and its blends: A review. Renew Sust Energ Rev 2010; 14(2): 667- 678.

[14] Johnson OC and Kummerow FA. Chemical Changes Which Take Place in an Edible Oil During Thermal Oxidation. J Am Oil Chem Soc 1957; 34: 407-409.

[15] Wexler H. Polymerization of Drying Oils. Chem Rev 1964; 64: 591-611.

[16] bondioli P, Gasparoli A, Lanzani A, Fedeli E, Veronese S and Sala M. Storage Stability of Biodiesel. J Am Oil Chem Soc 1995; 72(6): 699-702.

[17] R.O. Dunn. Effect of oxidation under accelerated conditions on fuel properties of methyl soyate (biodiesel). J Am Oil Chem Soc 2009; 79: 915–920.

[18] Jiayu Xin, Hiroaki Imahara, Shiro Saka. Oxidation stability of biodiesel fuel as prepared by supercritical methanol. Fuel 2008; 87(10- 11): 1807-1813.

[19] Robert O. Dunn. Effect of temperature on the oil stability index (OSI) of biodiesel. Energy Fuels 2008; 22 (1): 657–662.

[20] Nzikou JM, Matos L, Moussounga JE, Ndangui CB, Pambou- Tobi NP, Bandzouzi EM, Kimbonguila A, Linder M and Desobry S, Study of oxidative and thermal stability of vegetable oils during frying, Res J Ap Sci 2009; 4(2): 94-100.

[21] Pospisil J, Klemchuk PP, editors. Oxidation inhibition in organic materials. CRC Press; 1990. p. 1.

[22] Mittelbach M, Schober S. The influence of antioxidants on the oxidation stability of biodiesel. Journal of the American Oil Chemists Society 2003; 80: 817–23.

[23] Schober S, Mittelbach M. The impact of antioxidants on biodiesel oxidation stability. European Journal of Lipid Science & Technology 2004; 106:382–9.

[24] Liang YC May CY, Foon CS, Ngan MA, Hock CC, Basiron Y. The effect of natural and synthetic antioxidants on the oxidative stability of palm diesel. Fuel 2006; 85: 867–870.

[25] Sarin A, Arora R, Singh NP, Sharma M, Malhotra RK. Influence of metal contaminants on oxidation stability of Jatropha biodiesel. Energy 2009: 1-5.

[26] Domingos AK, Saad EB, Vechiatto WWD, Wilhelm HM, Ramos LP. The influence of BHA, BHT and TBHQ on the oxidation stability of soybean oil ethyl esters (biodiesel). Journal of the Brazilian Chemical Society 2007; 18.

[27] Sendzikiene E, Makareviciene V, Janulis P. Oxidation stability of biodiesel fuel produced from fatty wastes. Polish Journal of Environmental Studies 2005; 14 (3): 335-339.